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### THE COMPRESSIBILITY OF FIVE GASES TO HIGH PRESSURES.

BY P. W. BRIDGMAN.

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(Continued from page 3 of cover.)

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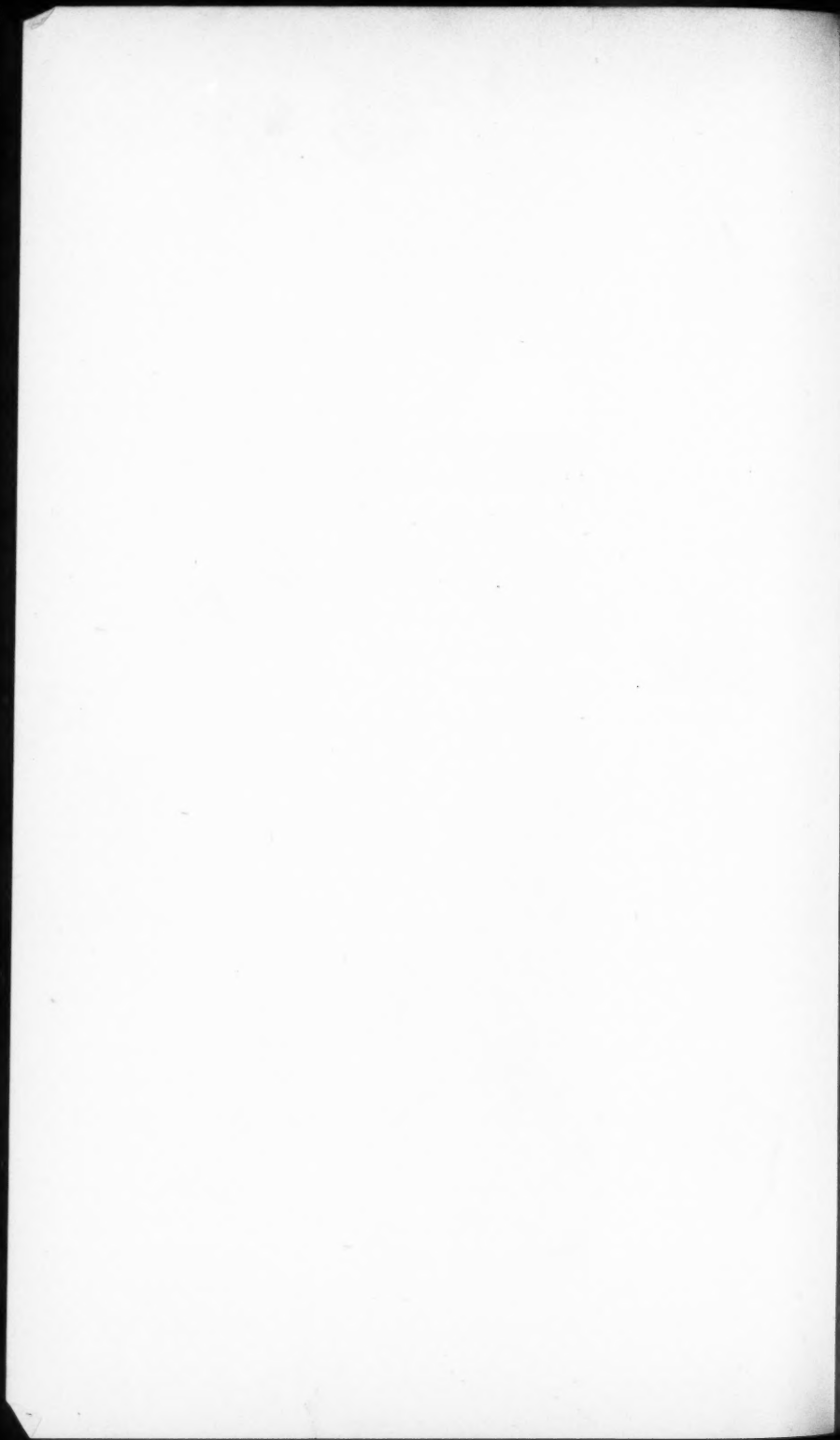
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## INTRODUCTION.

THE following represents the results of a first attack on the problem of determining the compressibility of gases to pressures of the same general magnitude as I have reached in my other high pressure work; in this case the pressures reached 15000 kg/cm<sup>2</sup> or more. It would probably be possible to improve on the results given here; my reason for giving results not the best that can be possibly obtained is that this matter of measuring the compressibility of gases to high pressures turned out to be of unexpected difficulty, and my various attempts to find a suitable method have already occupied three years. The error in the results to be given here I believe to be not more than a few per cent, and the results have seemed to me to be of sufficient interest to justify their publication, particularly as it may be some time before I am able to make a more successful attack on the problem.

The gases which I have measured are: hydrogen, helium, nitrogen, ammonia, and argon. The results for the monatomic gases helium and argon should be of particular significance in connection with recent speculations on the constitution of the atom.

The measurements given in the following are of the change of volume in cc. per gm. of gas as a function of pressure reckoned from 3000 kg/cm<sup>2</sup> as the initial point. For values of the absolute volume per gm.

the work of other observers at low pressures, up to 3000 kg/cm<sup>2</sup>, must be relied on. Direct measurements seem to have been made only for hydrogen and nitrogen (by Amagat<sup>1</sup>); for the other gases more or less probable values of the absolute volume at 3000 kg. must be obtained from equations of state which fit the data as well as possible over the low pressure range previously measured.

#### THE METHOD.

It will perhaps be of some interest to outline briefly the methods which were tried at first without success.

The apparatus used in all the attempts at measuring the compressibility of gases differs from that used in measuring the compressibility of liquids or solids<sup>2</sup> in that it was considerably smaller. This was primarily for reasons of safety, so that it would not be necessary to handle large volumes of gas, with the danger from explosions to be expected from the ruptures that almost always take place in this high pressure work. There was further an incidental advantage in using small apparatus in that the cylinders could be heat treated to higher elastic properties, so that higher pressures could be reached. 15000 and sometimes 16000 kg/cm<sup>2</sup> were reached in this work, against the more usual 12000 of my previous work.

The first attempt employed the simplest possible modification of the method which I have already used for the compressibility of liquids.<sup>2</sup> The gas was enclosed in a steel cylinder provided with a pressure gauge, and the pressure was produced by pushing a leak-proof piston into the cylinder. The compressibility is given by the change of volume, which is given by the motion of the piston. In order to reach pressures at all high, it is of course necessary to start with the gas at a rather high initial pressure. The necessity of providing this initial pressure in the gas distinguishes in one respect the technique of gas compressibility measurements from that of liquids. In the first form of apparatus the gas at high initial pressure was admitted through a bye-pass situated at the upper end of the cylinder, and closed off by the advance of the piston. The original source of the gas was a steel bottle in which the pressure was about 150 kg/cm<sup>2</sup>. This gas was admitted to an intensifier of the same design as that already used for liquids; the intensifier allowed an initial pressure of 2000 kg/cm<sup>2</sup>.

Attempts were made to measure in this way the compressibility of hydrogen and air, since these could be easily obtained compressed into steel bottles. Almost immediately a fundamental limitation of the

method was found for hydrogen, namely the steel cylinder will not withstand a pressure of more than about 9000 kg/cm<sup>2</sup> of hydrogen. Above this pressure the hydrogen escapes through the steel walls of the cylinder with explosive violence. The cylinders used had an external diameter of 2 inches and an inside diameter of  $\frac{1}{4}$  inch. The first escape of the gas is through a fissure so fine that it is impossible to find it even with moderate magnifying power, and the correct explanation was not at once obtained. However, after recharging the cylinder a number of times, and repeating the effect every time, the fissure finally grew to a size large enough to see with the naked eye. The effect was repeated on other cylinders. There is no possibility of the effect being due to a flaw in the steel, because the cylinders had been previously tested with a liquid to a pressure of 25000 kg/cm<sup>2</sup>. The action of the hydrogen is very similar to that which I have previously found with mercury.<sup>3</sup> The maximum pressure of mercury that steel will support is about 6000 kg/cm<sup>2</sup>, lower than for hydrogen. The action in the case of mercury was due to a combination of an opening of the pores of the steel by the pressure and the same chemical affinity between mercury and steel which manifests itself in amalgamation, if the steel surface is perfectly clean. There is no action between mercury and steel at high pressures unless the pores of the steel are distended by the pressure so that the mercury can enter. Steel vessels containing mercury can be used with perfect freedom under high pressure provided that the vessel is subjected to a hydrostatic pressure all over, thus producing a uniform volume compression, with closing instead of opening of the pores. The same sort of an effect I anticipated for hydrogen, and it will be seen in the following that some success was obtained by enclosing the hydrogen in a vessel subjected to hydrostatic pressure all over. The fact that the pressure of failure with mercury is less than that with hydrogen is doubtless partly explained by the fact that the size of the hydrogen molecule is greater than that of the mercury atom (the molecular volume of hydrogen even in the condition of greatest density now known is greater than that of mercury at atmospheric pressure), but this is not the whole story, for the molecular volume of helium is less than either hydrogen or mercury, and there is no similar penetrating effect. The element of chemical affinity is probably also necessary.

After the failure of the simple method with hydrogen, I spent much time trying for measurements with air. There was no such rupture effect as found with hydrogen, but the results were always inconsistent; and frequently could be apparently explained only by a slight leak,

although the entire apparatus was placed under water, and no leak could be ever detected externally. Finally, after being used a large number of times, the cylinder ruptured at about  $13000 \text{ kg/cm}^2$ . There seems to be an effect with air like that with mercury and hydrogen, but very much slower. It is probable that the irregular results which simulated leak were due to an actual absorption of the air by the steel walls of the cylinder. In addition to this effect, there is some chemical action, as was found in an attempt to measure the compressibility of air with the final form of apparatus. The high pressure air oxidizes the manganin of the pressure measuring coil, permanently changing its resistance, and also slightly oxidizes the silk insulation with which the wire is wound, giving a slightly charred appearance, and damaging the insulating properties.

The method having failed with hydrogen and air because the gas actually enters the pores of the metal, it appeared to me probable that the same effect would be found as a source of error with all gases, although very probably to a much less degree with some, and I discarded the method with regret, for its simplicity and directness.

The next method adopted was patterned in some ways after methods which have at times been used for the compressibility of both liquids and gases. Carnazzi,<sup>4</sup> for example, has employed a method for measuring the compressibility of liquids in which the liquid is compressed along a uniform tube by a rising column of mercury, and the height of the mercury is determined in terms of the resistance of a fine wire stretched along the axis of the tube and short-circuited by the advancing mercury and so reduced in resistance. It did not appear feasible to use a wire stretched along the axis of the tube in this case because of the necessarily small dimensions, and I modified the scheme by using a metal instead of a glass tube, and measured the total resistance of the tube between the two ends. The walls of the tube were thin, so that the resistance of unit length of mercury was much less than the resistance of unit length of the tube itself, thus allowing the position of the mercury to be obtained accurately from the measured resistance. It was necessary to fit the lower end of the tube with a reservoir into which a supply of gas at an initial pressure of several hundred  $\text{kg/cm}^2$  was forced, the reservoir being of such dimensions that the gas should be all compressed into the capillary by  $2000 \text{ kg}$ . This reservoir had to be fitted with a valve, and a method of filling devised. The tube was a steel capillary of about  $0.100 \text{ inch}$  ( $0.254 \text{ cm.}$ ) inside diameter, and walls  $0.003 \text{ inch}$  ( $0.0076 \text{ cm.}$ ) thick, especially drawn for this purpose.

Preliminary tests of the apparatus at low pressures of a few atmospheres gave satisfactory results, but I was never able to get any consistent results at high pressures, although a number of modifications were made, and much time was spent at it. The trouble is that the contact between the mercury and the steel wall of the capillary is capricious. Amalgamating the inside of the tube did no good. Apparently the trouble is that at high pressures any oxygen or water vapor present as a slight impurity in the gas, and of course all the more if air or oxygen is originally used, attacks the metal wall of the capillary, or perhaps the advancing mercury column, so that a film of oxide is deposited between the walls and the mercury, preventing contact. The walls of the tube were almost always found dirtied after exposure to pressure, although there was no trace of such action near atmospheric pressure. The method was finally abandoned.

I finally returned to the method used for liquids, but modified as follows. The gas is placed in a separate container, initially under a pressure of 2000 kg/cm<sup>2</sup>, and the container is surrounded by the kerosene with which pressure is transmitted. In this way direct contact of the gas with the walls of the cylinder and the consequent rupturing effect is avoided. The method is very much like that which I have previously used in determining the freezing curve of carbon dioxide.<sup>5</sup>

The final apparatus is shown in Figure 1. The gas container is the steel bomb B, closed at the lower end with an inward opening valve V. The bomb is charged to an initial pressure of about 2000 kg/cm<sup>2</sup> and the valve V closed, after which it maintains itself tight by the internal gas pressure. The quantity of gas is determined by weighing the bomb before and after filling. In order to obtain sufficient capacity, it is necessary that the walls of the bomb be as thin as consistent with safety. It can be understood that the explosion of the bomb, during the handling incident to filling and weighing, with an internal gas pressure of 2000 kg., might be a serious matter. The design must be such as to give as large a margin of safety as possible. The bomb was

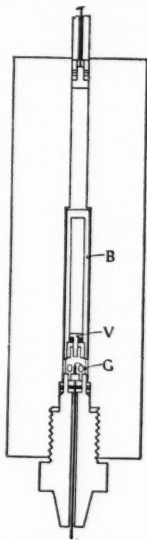


FIGURE 1. Cross section of apparatus for measuring compressibility of gases. The gas is contained in the bomb B, which is closed initially by the valve V. Pressure is measured with the manometer gauge G.

made of the same chrome vanadium steel as the outer cylinder, heat treated, and tested with fluid pressure to 4000 kg. I have never had trouble with the rupture of the bomb except when it had become weakened by contact with hydrogen, as will be explained later.

The bomb is filled with an auxiliary arrangement of design sufficiently obvious, so that it need not be described in full detail. The source of gas is a compressed steel bottle, with an initial pressure of between 100 and 150 kg/cm<sup>2</sup>. The bottle connects with the rest of the apparatus through a valve block, by which the bottle may be disconnected. The valve block connects with an intensifier of the same design as that used in my regular high pressure manipulations, in which the multiplication ratio is four to one, driven by a hand pump capable of giving 1000 kg/cm<sup>2</sup>. The pistons of the intensifier were packed with rubber, and were run dry, to avoid contaminating the gas. This packing has to be renewed very frequently, the wear on it being severe because of the lack of lubrication. The valve block also contains a manganin pressure gauge, connected with a Carey Foster bridge, with which the pressure in the gas produced by the intensifier may be measured. The valve block finally connects with another block in which is mounted the bomb, and which is provided with a stuffing box through which the valve at the lower end of the bomb is actuated by means of an extension stem screwing onto the thread at the lower end of the stem of the valve, shown in Figure 1, and projecting through the stuffing box. The valve has to be kept open with a screw during filling, as otherwise the internal pressure of the gas would close it. The procedure in filling is to open the connection to the gas bottle, with the piston of the intensifier in its extreme position, flush out the apparatus by admitting gas at the pressure of the bottle and blowing it out a couple of times at atmospheric pressure (or in the case of the rare gases argon and helium the interior of the apparatus is initially exhausted to a low vacuum through an auxiliary valve connection), the bottle is then shut off by the valve, leaving throughout the entire interior a pressure of 100 to 150 kg/cm<sup>2</sup>, and then the intensifier is actuated with the hand pump until the desired pressure of 2000 kg. is reached, as indicated by the manganin gauge. If the gas is very compressible, or if the initial pressure in the bottle is not high enough, it is necessary to use two intensifiers in parallel to get the requisite 2000 kg. This proved necessary for hydrogen and helium. It is necessary to guard carefully against leak during this filling; it is not possible with a stuffing box and a rod projecting through it to use the automatically tightening packing that I use in most high pressure



work,<sup>6</sup> and leak will occur unless care is taken with the packings. To guard against leak small air tight chambers are built around the outside of the strategic places, connecting with fine glass tubes which open under water, so that any leak is at once evident by bubbling through the water.

After filling to the required pressure the lower valve of the bomb is shut through the stuffing box, the bomb is removed from its receptacle, and the amount of gas determined by weighing. The weighing can be easily made to 0.0001 gm., the total weight being of the order of 30 gm., which means 0.1% on the weight of the lightest gas (weighing very nearly 0.1 gm.), and of course a greater proportional accuracy on the amount of the other gases. To avoid error in the weighing, the outside of the bomb is polished, and of course carefully cleaned before each weighing.

The bomb filled with gas is then placed in position in the pressure cylinder, which is now closed at the lower end by the plug with the manganin gauge, G, attached, as shown in Figure 1. The entire cylinder is now filled from the open upper end with the required amount of kerosene from a pipette provided with a stop cock. The filling takes place in three or four steps. A small amount of kerosene is first run in, and the cylinder exhausted through the upper end to a vacuum of about 0.5 cm. of mercury. When air is readmitted the kerosene is forced down into the crevices around the gauge and the bomb. This process is repeated, exhausting after every small addition of kerosene, until the required level is reached. The entire operation takes only a few minutes. The amount of kerosene is determined by weighing the pipette before and after filling. The kerosene used in all these measurements was taken from the same original lot, so that there is no error because of change in the quality of the kerosene.

The moving plug is now placed in the upper end of the cylinder. The packing of this plug is of the same design as used in my previous high pressure work, and is without leak. The only novel feature about the packing plug is that it is driven by a hollow piston. Through this piston projects a fine steel stem, soldered to the shank of the moving plug. This stem projects above the upper end of the hardened piston, and may be viewed with a reading telescope attached to a micrometer screw. A second reading telescope is set on a point fixed to the upper surface of the cylinder. The difference of reading of the two telescopes gives the amount of motion of the piston into the cylinder, and so the change of volume. Previously the motion of a point attached to the hardened piston was read.<sup>2</sup> The disadvantage of the former

method was that any wear of the packing is included in the apparent motion of the piston, whereas this is obviously avoided with the present modification.

The cylinder, filled as just described, was next mounted in the hydraulic press with which pressure was produced by pushing the piston into the cylinder. This press was a small one especially made for this work. The diameter of its piston is 1.625 inches (4.13 cm.) and it is driven by a hand pump of 1000 kg. capacity. Since the diameter of the small piston of the high pressure cylinder is 0.25 inch (.635 cm.), the multiplying power is 42 fold, thus permitting a maximum pressure of 42000 kg/cm<sup>2</sup>, without allowance for friction. The ram of the press is provided with the usual screw stop, so that the piston may be held in any desired position should the pressure of the hand pump be accidentally lost.

The lower part of the press with the cylinder in place dips into the temperature bath maintained at constant temperature by the conventional stirrer and regulator. The entire high pressure part of the apparatus is thus at the same temperature, and error is avoided due to volume changes when liquid passes from a part of the apparatus at one temperature to a part at another temperature.

Because of the small size of the apparatus, it was not possible to use the regular manganin pressure gauge which I have used in all the rest of my high pressure work.<sup>7</sup> To replace this gauge I procured from Baker and Co. some special American manganin wire 0.0035 inch (0.0087 cm.) in diameter and double silk covered, instead of the German manganin 0.0055 inch (0.0140 cm.) in diameter which I have previously used. Using the smaller size wire, it was possible to fit into the space at my disposal a coil of the usual resistance, 120 ohms. This American manganin was carefully seasoned before using by a long exposure to 140° and several applications of 16000 kg/cm<sup>2</sup>, but in spite of every care in preparing the coils, it was always much less satisfactory in its behavior than the regular German manganin. This may possibly have been due to the fact that the German manganin was 25 or more years old, but I believe was more probably due to an intrinsic difference in the material.

Several coils were made of Baker's manganin, and they were calibrated against the standard at each of three temperatures, 30°, 65°, and 95°, at which it was intended to make the measurements. The inferiority of the new material showed itself in a shift of the zero after an application of high pressure. This shift persisted throughout all the work, and showed no tendency to become less as the coil became

better seasoned. It was spasmodic and without predictable element. In extreme cases the zero shift might amount to the equivalent of 300 kg/cm<sup>2</sup> on the pressure, or 2% of the total pressure range. This amounts to only about 0.05% on the total resistance, but since this pressure gauge depends on small differences of resistance, it constitutes a serious objection to this material for pressure gauges. I attribute by far the greater part of the error in my final results to trouble with the pressure gauge. The remedy is to return to the German manganin gauge, using a shorter length of wire, and to improve the sensitiveness of the electrical measurements to compensate for the decrease of resistance of the coil. As a matter of fact, I have already done this, and have measured in this same apparatus the compressibility of some of the more compressible solids with much better results.

Runs were made at three different temperatures of the bath, as it was part of the program to obtain the thermal expansion of the gas as a function of pressure as well as the compressibility. At any fixed temperature the procedure consisted of first pushing the piston in by small amounts, starting with zero pressure, and plotting the piston position as a function of pressure. When the pressure in the kerosene rises as high as the pressure of the gas within the bomb, the valve at the lower end of the bomb opens inward, admitting the kerosene to compress the gas, which from here on takes part in the compression. The opening of the valve is shown by a discontinuity in the slope of the curve of volume against pressure, the gas of course being more compressible than the exterior of the steel bomb. After the valve opens into the bomb, pressure is pushed in a few large steps to the maximum to which it is intended to make measurements, in order to season the cylinder and take the give out of the various packing appliances. After the first maximum, pressure is then lowered in small steps to the pressure of discontinuity, or as near it as the friction of the moving plug will permit, and is then raised again in small steps to the maximum, determining at each of these steps the position of the piston as a function of pressure. By making readings with both directions of motion of the piston, error from hysteresis, which might be considerable, is avoided. The mean of readings with increasing and decreasing pressure is taken as giving the correct relation between pressure and volume. The same process is now repeated at another temperature, except of course the preliminary cautious manipulation in opening the bomb is no longer necessary. The pressure must not be allowed to fall so low after the valve has been once opened that the gas can expand into the part of the apparatus beyond the bomb.

## CORRECTIONS AND COMPUTATIONS.

The change of volume given by the motion of the piston as a function of pressure consists of two parts, one part due to the gas, and a second part including the change of volume of the kerosene, of the steel of the bomb, and the distortion of the cylinder. This second part may constitute one half of the total effect, and must be eliminated. The same method was adopted for doing this that was previously used for liquids. Blank runs were made with the gas replaced by a dummy steel core. If the amount of kerosene is the same in the two runs, the difference of the piston displacement of the two runs gives at once the difference of compressibility between the gas and steel, except for the small correction for the elastic change of bore of the cylinder. The compressibility of the steel is known, so we have at once the compressibility of the gas. But it was not possible to use exactly the same amount of kerosene in the two runs, so that a correction was necessary for the difference. This was determined by making two sets of blank runs, with different sizes of steel cores, and different fillings of kerosene, giving by difference the correction for kerosene. This correction was in all cases small, amounting to not more than one tenth of the major correction. The blank runs were of course made at each of the three temperatures, and the corrections were determined as a function of temperature.

The cross section of the cylinder increases at the higher pressures. This correction I did not attempt to determine directly, but calculated it from the theory of elasticity; I have fully discussed it in a previous paper.<sup>8</sup> I used the same formulas as previously, and the same numerical values of the elastic constants, as these constants are known to change very little with the grade of steel. The correction at the maximum amounts to about 1.0%.

The manganin gauge was calibrated at the three temperatures; at 95° the proportional change of resistance for a fixed pressure was 1.3% greater than at 30°. The linear relation between pressure and change of resistance has been established by direct measurement only to 13000 kg.<sup>7</sup> Within this range the linearity holds to better than 0.1%. It was assumed that the relation would remain linear through the additional range of this work, to 15000 or 16000 kg. The extension is so relatively slight as to occasion no uneasiness on this score.

When I began the measurements by this method I anticipated a serious source of error in the solution of the gas into the kerosene. This did not turn out to be at all important, however, as was shown in

two ways. In the first place, the position of the piston at the maximum pressure on the second application was almost exactly the same as on the first. The first maximum was reached rapidly, so that there was little time for the gas to diffuse through the liquid, whereas the second application was after an hour or more, when there had been more chance for diffusion. If the solution of the gas into the kerosene takes place with change of total volume, then the piston at the second maximum should not be in the position of the first, but would presumably indicate a smaller volume. In the second place, the amount of gas in solution would be expected to be a function of pressure, so that after every change of pressure there should be a gradual change in the amount of gas in solution, either coming out of solution or going in, according as the pressure change is a decrease or an increase. This change in the amount of gas in solution should be shown by a pressure creep. Such a pressure creep was never found, but equilibrium after a change in the position of the piston was always reached in a very short time, usually less than three minutes. The rapid attaining of temperature equilibrium after a change of pressure is due to the small size of the apparatus, and the fact that a large part of the interior of the cylinder is filled with metal; it constitutes an additional very considerable advantage of the small scale high pressure apparatus.

Because of the necessity of starting with an initial pressure of 150 kg., to carefully purify the gases would have required an especially elaborate arrangement, which was beyond my resources. I therefore used the best gases commercially obtainable, and corrected my results by means of the analysis of the gases, assuming in making the correction that the volume of the impurity was additive. This assumption should not be seriously wrong for those gases which have little tendency to chemical action on each other, and since the gases were quite pure to begin with, the error introduced in this way should in any event not be important. The details will be found under the separate descriptions.

The method of computation was as follows. The true motion of the piston was first found from the difference of reading of the upper end of the piston and the fixed point on the cylinder. The results at each temperature were then plotted on a large scale, and a single smooth curve drawn between the ascending and descending branches. The difference between the two branches, due to hysteresis in the metal parts, was of the order of 1.5% at the middle of the range, and of course vanishes at the two extremes. From the smooth curve the position of the piston was read at even thousand kilograms. The points

obtained in this way from the curve were now smoothed so as to give smooth first differences corresponding to the number of significant figures retained (four). These positions were now subtracted from that at 3000 kg., which thus became the fiducial pressure from which the changes of volume were calculated. In most cases it was not possible to reach much below 3000, and in any case, because of the steepness of the curve, the results below 3000 were not as accurate as above. The piston displacements were now corrected with the results of the two sets of blank runs, as already described, so that the displacement of the piston due to the gas alone was obtained at even thousands, with 3000 as the fiducial pressure. This displacement is that due to the weighed amount of gas. This was converted into the amount per gm. by multiplying by the proper factor, and this again into cc. per gm. by the cross section of the cylinder corrected for the distortion under pressure. The cross section of the cylinder was obtained by weighing the mercury which filled it to various depths, a special arrangement having been made for filling different lengths of the bore full without error from capillary effects at the end surfaces. The bore proved uniform over the entire length to the order of accuracy.

This calculation of the change of volume in cc. per gm. from 3000 kg. as the fiducial point was repeated for each of the runs at different temperatures and for each of the fillings of the apparatus, when more than one filling was made, as was usually the case. I had hoped to get from the measurements both the compressibility and the thermal expansion, but unfortunately in many cases the agreement between the different runs was not sufficient to give acceptable values of thermal expansion. What was usually done was to take the mean of all the sets of values for different temperatures and different fillings to give the best relation between pressure and change of volume at the mean temperature, which is approximately  $65^{\circ}$ . This strictly assumes that the relation between temperature and volume at constant pressure is linear. The temperature range is so small and the pressures are so high that no appreciable error can be introduced in this way.

In this way a relation between volume and pressure was obtained representing the mean of six or more runs. The details of the data, and the probable error of the mean will be found in the discussion for the different gases. In some cases it was possible to obtain values for the thermal expansion to which some degree of credence may be attached.

## DETAILED DATA.

*Hydrogen.* The material was obtained from the Boston Electrolytic Oxygen Co. The purity was high, it being stated that there was less than 0.1% of impurity. I made no analysis myself, but the general validity of this figure has been checked by analyses made in the Cryogenic Laboratory at Harvard University on hydrogen from the same source. The results given in the following are without correction for the effect of any impurity.

I have already given a brief account of the measurements on hydrogen in the Schreinemakers Festschrift.<sup>9</sup> The measurements gave much more trouble than with any other gas, the reason being the action between hydrogen and the steel cylinder. I have already described how it was impossible to use the hydrogen directly in the cylinder because of penetration of the steel by the hydrogen and rupture of the cylinder. The same effect was found to a much more limited extent in the final arrangement. Although the hydrogen is prevented by the kerosene from coming directly into contact with the steel, the hydrogen goes into solution in the kerosene and attacks the steel from solution. The action is much slower than when the hydrogen comes into direct contact, and it was possible to obtain a few measurements to high pressures, but not as many as with the other gases. The action between hydrogen and steel is not like in all respects that between mercury and steel. A piece of steel surrounded on all sides by mercury and exposed to hydrostatic pressure exerted by the mercury absorbs no mercury into its pores, which are closed by the pressure, and after removal of the pressure the steel returns to its original state in every respect. But if a piece of steel is surrounded by hydrogen, or by kerosene in which hydrogen is dissolved, and subjected to hydrostatic pressure, the hydrogen dissolves in the steel in spite of the closing of its pores, and very seriously weakens the steel. The action was shown by the weakening of the bombs in which the hydrogen was initially compressed to 2000 kg., and of other steel parts. After an excursion to high pressures the bomb was often weakened or even ruptured, so that it would not support a second filling. One of these bombs exploded during manipulation previous to weighing after the second filling, but luckily with no serious consequences, the fracture taking the form of an open seam down the side with no flying fragments. Once or twice the bottom was separated from the rest of the bomb. Four or five bombs were used altogether. Other parts of the apparatus were also weakened: the valve stem ruptured



several times, the stem of the moving plug pinched off several times after a run with hydrogen, and finally the large outer cylinder itself ruptured after a number of runs to high pressures. At this point the experiments with hydrogen were discontinued, since I already had a few measurements to high pressures, and the uncertainty and danger in the experiment did not seem to justify further experiment. Steel which has been acted on by hydrogen is quite altered in appearance, the fracture being coarse and crystalline instead of fine and silky as is characteristic of high grade alloy steel.

Runs to high pressures were obtained with two fillings of the apparatus. The first filling gave complete runs between 2000 and 13000 kg/cm<sup>2</sup> at 30° and 65°, and also a fragment of a run at 95°, which was terminated by fracture of the stem of the moving plug. The second filling gave an incomplete run at 30° between 2000 and 14000 kg. This run was terminated by the rupture of the large cylinder; for this reason the high pressure results of this run are not to be accepted, as it is not unlikely that there was some unusually large distortion of the cylinder before rupture, but the measurements at the low pressure end of this run agreed exactly within the sensitiveness of the measurements with the other run. In fact, the agreement between the two runs is much better than for the average of the other gases, which gave no trouble with rupture.

The results are collected in Table I. The data obtained directly from experiment are the changes of volume from 3000 kg. as the fiducial pressure, which are shown in Columns 2 and 3. In order to obtain the actual values of volume I have assumed Amagat's volumes<sup>1</sup> at 3000 at 30° and 65°. The actual volumes calculated from Amagat's fiducial volumes are given in columns 4 and 5. In column 6 are given the values at 30° of  $p_v$ , in order to facilitate comparison with the method of presentation of Amagat. The pressure is here expressed in kg/cm<sup>2</sup> instead of in atmospheres, as does Amagat, and the volume is the volume of that quantity of gas which at 0° C. and 1 kg. pressure occupies 1 cc.

There is some question as to whether the fiducial volumes taken from Amagat are correct. This is suggested by the fact that in the range between 2000 and 3000, in which our measurements overlap, our results do not agree. His change of volume between 2000 and 3000 is 2.50 against 2.25 of mine. Furthermore, if  $p_v$  is plotted as a function of pressure it will be found that Amagat's value for 2000 lies off the smooth curve, although his 3000 point lies on it, whereas all of my points lie on the same curve. My value for the change of volume



TABLE I.  
RESULTS FOR HYDROGEN.

Pressure kg./cm <sup>2</sup>	Change of Volume cc. per gm. from 3000 kg.		Volume cc. per gm.		pv at 65°	Volume cc. per mol	
	30°	65°	30°	65°		at 30°	at 65°
2000	-2.25		13.89		2.54	27.99	
3000	0.00	0.00	11.64	12.17	3.18	23.47	24.53
4000	1.12	1.14	10.52	11.03	3.83	21.21	22.24
5000	1.84	1.88	9.80	10.29	4.50	19.76	20.74
6000	2.35	2.44	9.29	9.73	5.08	18.73	19.62
7000	2.77	2.88	8.87	9.29	5.65	17.88	18.73
8000	3.09	3.21	8.55	8.96	6.23	17.24	18.06
9000	3.38	3.46	8.26	8.71	6.17	16.65	17.56
10000	3.63	3.68	8.01	8.49	7.29	16.15	17.12
11000	3.86	3.88	7.78	8.29	7.80	15.68	16.71
12000	4.09	4.04	7.55	8.12	8.25	15.22	16.37
13000	4.32	4.21	7.32	7.96	8.66	14.76	16.05

between 2000 and 3000 agrees exactly with that which would be calculated by an empirical equation of Keyes,<sup>10</sup> which fits the other low pressure observations within the limits of error. In addition, the equation of Keyes fits my observations very well to higher pressures, as I will describe more in detail later. Of course if it should be established certainly at any future time that Amagat's results at 3000 are in error, the values in Table I can be simply corrected by an additive constant.

The values of the thermal expansion, to be obtained from the Table by taking the differences of volume between 30° and 65° are to be used with a certain amount of caution. I have already stated that the thermal expansions in general do not have the accuracy which I had hoped. It is nevertheless probable that the values for hydrogen are more accurate than the average, indicated partly by the smoothness of the data, and partly by the fact that my change of volume between 30° and 65° at 3000 kg. agrees exactly with that of Amagat. The values of the Table show a remarkable feature in that the expansion at 13000 kg. is greater than at 2000. Such behavior is not without precedent, however, as I have already found it for a number of liquids.

I believe, however, that in theoretical speculations it would be safest to ignore this apparent abnormality of the thermal expansion at high pressures. It will be found on a careful analysis of the data that the anomaly is entirely due to the shape of the isothermal at  $30^{\circ}$ . If the compressibility is plotted as a function of pressure, it will be found that beyond 8000 at  $30^{\circ}$  the compressibility remains nearly constant independent of pressure, whereas at  $65^{\circ}$  it continues to fall over the entire pressure range as is normal for other gases. (See page 199 of the following.) For this reason I have used in the following the isothermal at  $65^{\circ}$  as more probably accurate than that at  $30^{\circ}$ . Of course the possibility must be recognized that the abnormal isotherm at  $30^{\circ}$  may be connected with a real freezing of the hydrogen at high pressure, the freezing being very much rounded because of solution of the hydrogen in kerosene, but this does not appear to me to be a very probable explanation.

Further discussion of the results for hydrogen is reserved for the general discussion of all the data.

*Helium.* This was obtained from one of the cylinders prepared during the war for the American Navy. I have to thank Professor H. N. Davis for obtaining me this particular cylinder. It is known that the impurity in this helium is practically all nitrogen. Professor F. G. Keyes of the Institute of Technology was so kind as to analyze this gas for helium content, and found 95.8% by volume pure helium. I have assumed in applying corrections to the data that the remaining 4.2% was entirely nitrogen, and the corrections applied were obtained from the high pressure measurements on nitrogen. The correction amounts to about 20% of the observed piston displacements, since my results are given in terms of a weight instead of a volume analysis.

Three sets of runs in all were made with helium. The first did not give results of much value because the quantity of helium that could be got into the bomb was so small that it was not possible to reach more than 5 or 6000 kg. The reason for this was that the initial pressure in the steel bottle was much less than had been supposed, there having been obviously some leak after storing. This was remedied for the second and the third runs by using two intensifiers in parallel instead of one. The second filling gave enough gas to reach 12000 kg., but only the run at  $30^{\circ}$  gave reliable results. There was a leak at the end of the stroke at  $30^{\circ}$  due to my endeavor to reach too high pressures; in spite of the leak I continued the run at  $65^{\circ}$  and  $95^{\circ}$  hoping that the leak had been entirely kerosene, but the character of the results when finally computed showed that this could not have been the case, and

only the 30° results of this filling were retained. Helium is quite different from the other gases measured in its continued compressibility at high pressures, so that my preliminary estimates of the dimensions required turned out to be incorrect. The device of partly filling the interior of the bomb with a plug of steel and compensating for the decreased volume by a higher initial pressure made it possible to reach a pressure higher than on the second run. The third filling gave results without accident to 15000 kg/cm<sup>2</sup> at 30°, 65°, and 95°. The two runs at 30° of the second and third fillings did not give consistent results, but the changes of volume of the second filling, calculated from 3000 as the fiducial point, were consistently almost exactly 10% less than those of the third over the entire pressure range. There seems to be no good reason why the second run, before the leak developed, should not be as good as the third, and I have therefore averaged the results in the following way. The average of the three runs at 30°, 65° and 95° of the third filling was taken as the best value at 65° as determined by this filling, and this was then corrected by subtracting 5% in order to allow for the results with the second filling.

The values obtained for the thermal expansion of helium bear internal evidence of being fairly reliable; this internal evidence is the comparability of the thermal expansion between 30° and 65° with that between 65° and 95°. These two expansions are roughly the same over the entire pressure range; at the lower end of the range the expansion over the lower temperature range is somewhat larger than over the upper range, while the behavior is reversed at the highest pressures. Probably the variations are beyond the limits of error, and I have not tried to retain them in the final results.

In Table II are given in column 2 the volume decrements at 65° in cc. per gm. with 3000 kg/cm<sup>2</sup> as the fiducial pressure (this is the average calculated as explained), in column 3 the total thermal expansion between 30° and 95° in cc. per gm., in column 4 the volume at 65° in cc. per gm. and in column 5 the volume in cc. per gm. molecule, using as the fiducial volume at 3000 kg. the value given by Keyes' equation of state <sup>11</sup> (there are no experimental values to this pressure). The value given by the equation, which amounts to a rather wide extrapolation, is in some doubt, and is, I believe, too high, so that it is probable that helium is even more compressed than appears in the table. In the last column of the table is given the product  $p_v$ , pressure in kg/cm<sup>2</sup>, and  $v$  the volume in cc. of that amount of helium which under 1 kg. pressure and at 0° C. occupies 1 cc. (1/7210 gm.) Further comment on the values in the table is reserved for the general discussion.

TABLE II.  
RESULTS FOR HELIUM.

Pressure kg/cm <sup>2</sup>	Change of Volume cc. per gm. at 65°	Total Change of Volume 30° to 95° cc. per gm.	Volume at 65°		pv at 65°
			cc. per gm.	cc. per mol.	
3000	0.00	.613	5.54	22.16	2.31
4000	0.77	.598	4.77	19.08	2.64
5000	1.23	.589	4.31	17.24	2.99
6000	1.54	.584	4.00	16.00	3.33
7000	1.77	.581	3.77	15.08	3.66
8000	1.96	.579	3.59	14.36	3.98
9000	2.10	.578	3.44	13.76	4.29
10000	2.22	.576	3.32	13.27	4.60
11000	2.33	.575	3.21	12.84	4.89
12000	2.41	.574	3.13	12.52	5.21
13000	2.48	.572	3.06	12.24	5.52
14000	2.55	.571	2.99	11.96	5.82
15000	2.60	.570	2.94	11.76	6.11

*Ammonia.* I am indebted for the material to the kind offices of Professor A. B. Lamb, who made the suggestion, and Dr. A. T. Larsen of the Fixed Nitrogen Research Laboratory, who furnished the material. It was provided in a small steel bottle, and was of exceptional purity, the only impurity being not more than 0.001% of water vapor. Because ammonia is liquid at low pressures, it was not necessary to use the intensifier arrangement for filling, but the ammonia was distilled across from the bottle, which was maintained at 95°, into the bomb, which was maintained at 0°. The connecting pipes were of course exhausted before filling, and were also flushed out with a preliminary filling of ammonia.

Owing to unexpected chemical difficulties, only a few readings were obtained with this substance. At 30° with the first filling a run was made to 12000 kg. which appeared satisfactory in every respect. On trying for the run at 65° there were minor irregularities in the pressure readings, which became very much accentuated at 95°, the behavior being exactly like that when the coil has been accidentally short circuited with water, the resistance decreasing and there being

polarization effects. A second filling was now made, and I tried the runs in inverse order, thinking that perhaps the polarization effect was something that gradually developed after the ammonia had stood in contact with the kerosene at high pressures. At 95°, however, there was this time at the very beginning, as soon as the apparatus was brought to temperature, and while the pressure was not more than a few hundred kilograms, a creep of the zero amounting to a pressure change of a couple of thousand kilograms. Equilibrium was reached after several hours, and a run was made, with no such trouble from polarization as had been found before. Then the temperature was lowered to 65°, when polarization appeared to such an extent that readings could not be made. The polarization persisted on lowering the temperature to 30°. The apparatus was taken apart, the ammonia of course evaporating into the atmosphere, and the polarization completely disappeared. It is evident that no water had accidentally got into the coil, but that the effect is in some way connected with the ammonia. The chemists with whom I have talked seem to think that no direct chemical action is to be expected, but the physical evidence seems strong that either the ammonia dissociated enough to conduct electrolytically, or else that some volatile compound was formed that is an electrolytic conductor.

The uncertainty of the pressure measurements made it possible to retain only the readings at 30° of the first run. The results of this run are given in Table III. At 30° the change of volume reckoned from 3000 kg. as the fiducial pressure is given in cc. per gm. and also in cc. per gm. molecule. It is to be noticed that it was possible with ammonia to make readings to considerably lower pressures than with the "permanent" gases, the volume readings reaching down to 1000 kg. The reason for this was that since ammonia is a liquid under slight pressure, the initial pressure in the bomb was low, and only a small pressure was required to open the valve. There seem to be no adequate low pressure measurements from which the fiducial volume at 3000 (or even at 1000) kg. may be extrapolated, so that I have not attempted to give in the table the absolute volumes.

*Nitrogen.* This was obtained from the Air Reduction Co., through the kindness of Professor H. N. Davis. It was of an especially pure grade, O<sub>2</sub> not more than 0.2% and argon probably about 0.16%. No corrections were applied for impurity.

Runs were made with four fillings of the apparatus. The first filling gave runs at 30°, 65°, and 95°, apparently successful in every way, and the best runs of the series. With the second filling I tried

for the runs in inverse order, in order to eliminate as far as possible effects due to irregularities in the zero shift of the manganin pressure gauge. A successful run at  $95^\circ$  was obtained, but on passing to  $65^\circ$ , there was leak due to rupture of the stem of the moving plug, which had been rotted by previous exposure to hydrogen. The third filling gave another successful run at  $95^\circ$ , but again on trying for  $65^\circ$  there was leak, this time because the piston was pushed in too far in the

TABLE III.  
RESULTS FOR AMMONIA.

Pressure kg/cm <sup>2</sup>	Change of Volume at $30^\circ$	
	cc. per gm.	cc. per mol.
1000	-.827	-14.1
1500	-.400	- 6.81
2000	-.217	- 3.70
2500	-.088	- 1.50
3000	.000	0.00
4000	.120	2.04
5000	.200	3.41
6000	.261	4.44
7000	.310	5.28
8000	.348	5.93
9000	.380	6.48
10000	.409	6.97
11000	.436	7.42
12000	.461	7.85

attempt to get too high pressures. The fourth filling gave successful runs at  $65^\circ$  and  $30^\circ$ . These runs were not as consistent as would have been desirable. The greatest inconsistency was at  $95^\circ$ , where the extreme variation amounted to 11%, at  $65^\circ$  the extreme variation was 7%, and at  $30^\circ$ , 4%. The average of the seven successful runs was taken to give the best value of the compressibility at the mean temperature,  $68^\circ$ .

The results with nitrogen were not regular enough to allow satisfactory values of the thermal expansion. The first run was the only one that gives even moderately regular values, and here the difference between the mean expansion per degree between  $30^\circ$  and  $65^\circ$  compared with that between  $65^\circ$  and  $95^\circ$  is so large as to be improbable.

In Table IV are collected the final results. In this are given the mean change of volume in cc. per gm. and in cc. per gm. molecule at  $68^\circ$ , reckoned from 3000 kg. as the fiducial pressure. These changes of volume are converted into the actual volume by using Amagat's value for the volume of 1 gm. of nitrogen at  $68^\circ$  and 3000 kg., namely 1.290. In the last column of the Table is given the values of  $p_v$ , the pressure being expressed in  $\text{kg}/\text{cm}^2$ , and  $v$  being the volume of that

TABLE IV.  
RESULTS FOR NITROGEN.

Pressure kg./cm <sup>2</sup>	Change of Volume at $68^\circ$		Volume at $68^\circ$		$p_v$ at $68^\circ$
	cc. per gm.	cc. per mol.	cc. per gm.	cc. per mol.	
2500	-.066	-1.85	1.356	37.98	4.11
3000	.000	0.00	1.290	36.13	4.68
4000	.089	2.49	1.201	33.64	5.82
5000	.152	4.25	1.138	31.88	6.89
6000	.197	5.52	1.093	30.61	7.95
7000	.234	6.56	1.056	29.57	8.95
8000	.264	7.40	1.026	28.73	9.94
9000	.287	8.04	1.003	28.09	10.94
10000	.308	8.61	.982	27.52	11.91
11000	.326	9.14	.964	26.99	12.84
12000	.342	9.60	.948	26.53	13.78
13000	.357	10.00	.933	26.13	14.70
14000	.370	10.36	.920	25.77	15.60
15000	.382	10.70	.908	25.43	16.50

amount of nitrogen (0.001211 gm.) which at 1 kg. pressure and at  $0^\circ$  C. occupies 1 cc.

It appears that just as in the case of hydrogen, Amagat's volume at 3000 kg. may be in doubt. For the difference of volume between 2500 and 3000 kg. I find experimentally 0.066 against Amagat's 0.070. The difference is in the same direction as for hydrogen, but less in amount. That there is a discrepancy between Amagat's data at low and high pressures has been shown in a thesis by L. B. Smith, entitled "The Equation of State and Some Related Quantities for Pure Nitrogen, Gas Phase," written at the Mass. Institute of Technology under the direction of Professor F. G. Keyes. I am indebted to Professor Keyes for an inspection of the manuscript. It appears that an equa-

tion of state fitting the low pressure observations with high accuracy gives somewhat smaller volumes at the high pressures than given experimentally by Amagat.

*Argon.* This again I owe to the kindness of Professor H. N. Davis, through whom it was secured from the Air Reduction Co., Special analysis gave 0.1%  $O_2$  and 1.0%  $N_2$ , unusually pure for a commercial product compressed into a steel bottle. In making the corrections, I have proceeded as if the entire impurity was 1.1% of  $N_2$ . Some such approximation is necessary in view of the fact that the compressibility of  $O_2$  to high pressures is not known. The approximation must fall well within the limit of error of the measurements, considering the small amount of impurity and the similarity of the molecular weights of  $O_2$  and  $N_2$ . The total amount of the correction was about 0.5%.

It was necessary to use a different high pressure cylinder for argon than for the other gases, the cylinder which had been used for the others having been ruptured by the last run with hydrogen. The new cylinder was of the same construction and dimensions as the first, and was seasoned and calibrated for bore and distortion by blank runs with fillings of steel and kerosene exactly as was the first cylinder.

Two fillings of the apparatus were made, and with each filling complete sets of runs at 30°, 65°, and 95° were obtained. The readings appeared perfectly smooth and in every way successful, but on working up the results numerically, considerable irregularities were evident. One of the runs at 95° lay so far away from the other, and what would be judged from the runs at the other temperatures to be the probably correct behavior, that it was discarded in taking the final average. There were left five runs, of which the average was taken to give the compressibility at the average temperature, 55°. The two runs at 30° differed by 7% from each other, and the two at 65° by 3%. The runs at the different temperatures are not consistent enough to justify the attempt to force from them numerical values for the thermal expansion. The following general statement about the behavior of the thermal expansion does seem to be justified, however, that the change of volume in cc. per gm. for a fixed temperature rise decreases very slightly at the high pressures, so that the relative thermal expansion increases at high pressures nearly inversely as the volume. This is the general type of behavior that has been found for hydrogen and helium.

The results for the change of volume in cc. per gm. and also in cc. per gm. molecule at the mean temperature 55°, reckoned from 3000



kg. as the fiducial pressure, are shown in Table V. In general, the volume falls off less rapidly at the high pressures than it does for hydrogen and helium, which is what would be expected from the larger atom of argon.

TABLE V.  
RESULTS FOR ARGON.

Pressure kg/cm <sup>2</sup>	Change of Volume at 55°	
	cc. per gm.	cc. per gm. atom
2000	-.083	-3.31
2500	-.034	-1.36
3000	.000	0.00
4000	.049	1.96
5000	.085	3.39
6000	.112	4.47
7000	.134	5.34
8000	.152	6.06
9000	.167	6.67
10000	.180	7.18
11000	.190	7.58
12000	.201	8.00
13000	.209	8.34
14000	.217	8.66
15000	.224	8.94

#### GENERAL SURVEY OF RESULTS.

In comparing the results for the different gases it is convenient to refer the measured changes of volume to the gram molecule (or gram atom) as the unit, since in the state of a perfect gas the volumes of all gases are equal per gram molecule.

In Figure 2 are shown the volumes per mol. of hydrogen, helium, and nitrogen as a function of pressure, these three being the only ones of the five gases measured for which we have a fairly reliable value of the volume at the fiducial pressure, 3000 kg. The absolute volumes of nitrogen and hydrogen are fairly certain, since these depend on the directly measured values of Amagat,<sup>1</sup> but the volume of helium at 3000 is much more in doubt, being taken from an equation of Keyes<sup>11</sup>

reaching to only 66 atmospheres. This will be discussed in more detail later; it is sufficient to state here that the fiducial value at 3000 assumed for helium is in all probability too high, so that the actual curve for helium should run lower than shown in Figure 2.

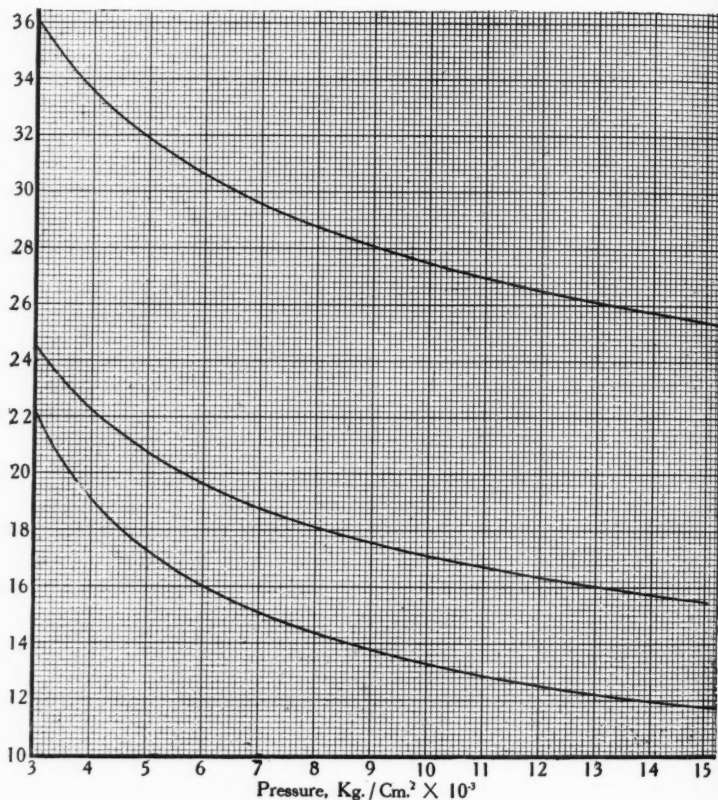


FIGURE 2. The volume in cc. per mol. as a function of pressure at 65° of nitrogen, hydrogen, and helium, reading from the top down.

Figure 2 brings out strikingly the great difference in the volumes per mol. of the different gases at high pressures, the variation from nitro-

gen to helium being by a factor of more than 2. The relative volumes are in the sequence which we would expect from the absolute dimensions of the molecules as given by the usual considerations of kinetic theory, as for instance, from the rates of diffusion. The diameter of the molecule of nitrogen thus found is the largest, and that of the atom of helium the least, and furthermore the difference of diameter between nitrogen and hydrogen is twice as great as the difference between hydrogen and helium, agreeing with the relative spacing of the curves shown in Figure 2.

It is interesting to compare the distances between the centers of the molecules (or atoms) at the highest pressure reached above, 15000 kg., with the molecular distances calculated from the ordinary kinetic theory. In Table VI are given the densities of the three gases at

TABLE VI.  
MOLECULAR DISTANCES AT HIGH PRESSURES COMPARED WITH  
MOLECULAR DIAMETERS.

Substance	Density at 15000 at 65°	Distance between Molecular Centers		Molecular Diameter from Kinetic Theory	
		Spheres Close Packed	Spheres Normal Cubic	Boyle's Law	Free Path
Hydrogen	.1301	$2.97 \times 10^{-8}$	$2.65 \times 10^{-8}$	$2.54 \times 10^{-8}$	$2.72 \times 10^{-8}$
Helium	.340	2.87	2.56	1.98	2.20
Nitrogen	1.102	3.89	3.47	3.56	3.80

15000 (extrapolated from 13000 for hydrogen), the distance between molecular centers, calculated on the assumption that the molecules are perfect spheres and (1) packed as closely as possible or (2) packed in simple cubical array, and finally the molecular diameter from kinetic theory calculated (1) from the deviation from Boyle's law and (2) from free path data. It will be seen that the molecules are compressed very nearly into what would be actual contact if they behaved like rigid spheres. The approach to the dimensions of contact is most close for nitrogen and least close for helium (the distance for helium would be diminished by using a more probable value for the fiducial volume). At distances approaching so closely to contact it seems

inevitable that the molecule ceases to behave like a rigid sphere, but must undergo considerable distortion which must be taken account of in framing a kinetic theory valid at such small volumes. It is also evident, of course, that the ordinary considerations of the kinetic theory valid at low pressures must be replaced by others of quite a different character. Thus the idea of a "free" path and simple molecular collisions is probably of little value when the molecules are so tightly packed.

By comparing the volumes of the gases under 15000 kg. with the volumes of the condensed phases at the triple points, we can set a lower limit to the compressibility of the solid or the liquid phase of these gases, a quantity which has never been measured experimentally, and for which we have no means, as far as I know, of guessing even the order of magnitude. The density of liquid hydrogen is given in tables as 0.070 at  $-252^{\circ}$ , and that of the solid as 0.076 at  $-259.9^{\circ}$ , both at approximately atmospheric pressure. Imagine that we compress solid hydrogen at a temperature of  $-259.9^{\circ}$  to a pressure of 15000 kg., and then raise the temperature at 15000 kg. to  $65^{\circ}$  C. We arrive at a substance of density 0.1301. During the last increase of temperature we have increased the volume for two reasons, first the ordinary temperature expansion, and second an increase of volume when the substance passes from the solid to the gaseous phase. It follows that the density of the solid at 15000 kg. and  $-259.9^{\circ}$  is certainly greater than 0.1301. Hence the compressibility of solid hydrogen is so great as to allow under 15000 kg. a decrease of volume to less (and probably much less) than 0.58 of its original value. This is certainly the highest compressibility that has ever been found in a solid; the greatest volume change in a solid that has hitherto been measured to my knowledge is that of potassium, which under 15000 would decrease to about 0.70 of its initial volume. In the same way by comparing the volume of the liquid at atmospheric pressure (density 0.070) with that of the gas under high pressure, we find that liquid hydrogen is so compressible as to allow under 15000 kg. a decrease of volume to less than 0.54 of its initial value. The most compressible liquid yet measured is ether;<sup>12</sup> this gives at 15000 (extrapolated from 12000) a decrease of volume to 0.66 of the initial value.

The compressibilities are even more extreme in the case of helium. The density of liquid helium at  $-271.6^{\circ}$  is 0.1456, that of gaseous helium at 15000 kg. at  $65^{\circ}$  is 0.340 (or greater). Hence liquid helium at  $-271.6^{\circ}$  is compressed by 15000 kg. to less than 0.43 of its initial volume, a truly astounding compressibility.

The figures for nitrogen are more conservative. The density of liquid nitrogen at  $-195^\circ$  is 0.810 and at  $-205^\circ$  0.854. The density of the gas at  $65^\circ$  at 15000 kg. is 1.102. The compressibility of the liquid, making no allowance for temperature expansion, is thus very close to that of the more compressible liquids hitherto measured. Allowing for the temperature expansion, the compressibility is probably greater than that of the most compressible liquid yet measured, but not much greater.

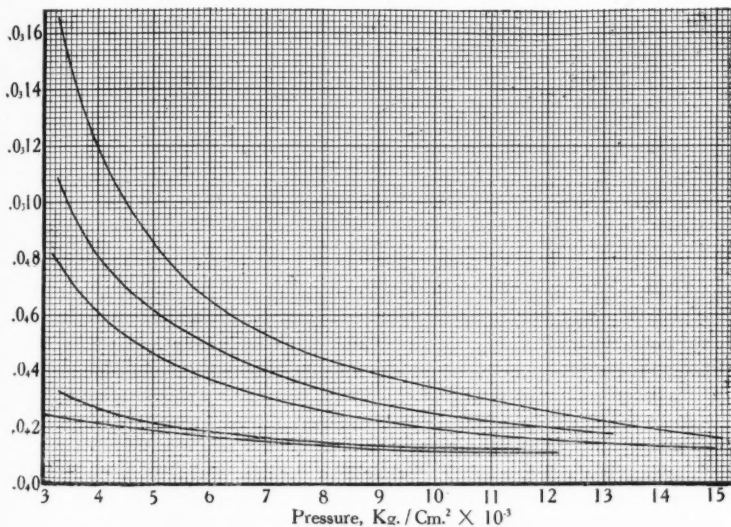


FIGURE 3. The compressibility,  $\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_\tau$ , as a function of pressure, of helium at  $55^\circ$ , hydrogen at  $65^\circ$ , nitrogen at  $68^\circ$ ,  $\text{CS}_2$  at  $65^\circ$ , and water at  $65^\circ$ , reading from top down.

A further idea of the behavior of these high pressure gases as compared with the ordinary liquid is given by a study of the compressibility. This is shown as a function of pressure in Figure 3 for hydrogen at  $65^\circ$ , helium at  $55^\circ$ , and nitrogen at  $68^\circ$ . The compressibility thus shown is the quantity  $\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_\tau$ . This quantity is not exactly the same as that which I have previously called the compressibility, which I

have usually defined as  $\frac{1}{v_0} \left( \frac{\partial v}{\partial p} \right)_\tau$ , where  $v_0$  is the volume at atmospheric pressure. The change in the convention is necessary when dealing with gases because of the very large  $v_0$  of a gas. In the same diagram are also shown the compressibility of two liquids, water and  $\text{CS}_2$ , defined in the same way as for the gas. It will be seen that under high pressures the compressibility of gases behaves in very much the same way as that of substances ordinarily liquid. At 5000 kg. the compressibility of nitrogen is the same as that of water at atmospheric pressure; hydrogen reaches this figure at 6000 kg., and helium at 7500.

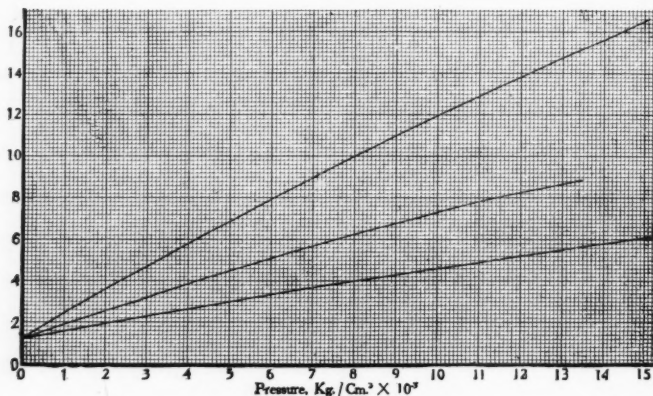


FIGURE 4. The product  $pv$  as a function of pressure for nitrogen, hydrogen, and helium (curves reading from top down).  $p$  is the pressure in  $\text{kg}/\text{cm}^2$  and  $v$  is the volume of that weight of gas which under a pressure of  $1 \text{ kg}/\text{cm}^2$  occupies  $1 \text{ cc}$  at  $0^\circ \text{C}$ . The temperatures are as in Figure 3.

From here on the decrease of compressibility is rapid, the high pressure gas behaving like an ordinary liquid at somewhat lower pressures. The diagram gives the impression that at pressures not very much in excess of 15000 the compressibility of the three gases and the two liquids will be very much the same. The order of sequence of the compressibilities of the three gases is what would be expected from the molecular volumes, the compressibility of helium being greatest and that of nitrogen least. (Lowering the fiducial volume at 3000 of helium would increase its compressibility by a factor becoming greater at the higher pressures.)

Carrying out the method of presentation of Amagat, I have shown in Figure 4 the product  $p_v$  as a function of pressure. For a perfect gas,  $p_v$  has the constant value 1.24 at  $65^\circ$ . The three gases are seen to behave quite differently in this regard; as before helium is most compressible (that is, it approaches most closely to the perfect gas),

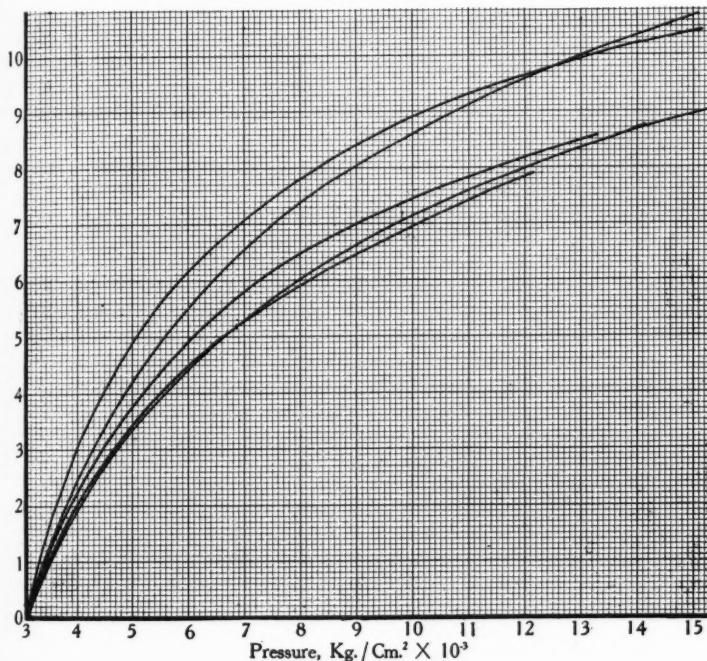


FIGURE 5. The change of volume in cc. per mol. as a function of pressure reckoned from  $3000 \text{ kg/cm}^2$  as the fiducial pressure. At  $10000 \text{ kg/cm}^2$  the order of the curves, reading from top down, is: helium at  $55^\circ$ , nitrogen at  $68^\circ$ , hydrogen at  $65^\circ$ , argon at  $55^\circ$ , and ammonia at  $30^\circ$ .

hydrogen is intermediate, and nitrogen is least. As a function of pressure,  $p_v$  is nearly linear, but with a quite definite downward curvature. Possibly the simplest way to derive an equation of state would be to reproduce these curves. I have found that an ordinary



two constant power series in the pressure is not adequate within the experimental accuracy.

Turning now to the other two substances, ammonia and argon, whose fiducial volumes at 3000 I have not tried to estimate, a certain amount of information, although not as much as for the other substances, may be obtained from a study of the changes of volume above 3000. In Figure 5 are plotted the volume changes in cc. per mol. reckoned from 3000 as zero, including in the diagram also the volume changes of hydrogen, helium, and nitrogen. The volume changes of all five substances do not differ very much from each other. The changes for ammonia and argon are slightly less than for the others. There are two cases of crossing of these curves; the curve for nitrogen crosses that of helium near 13000 kg., and that of argon crosses that of ammonia near 5500 kg. It is also evident that argon would cross hydrogen not far beyond the pressures actually reached. It seems to me that the explanation of these crossings is to be sought in the compression of the structure of the atom or the molecule itself. Compare, for instance, nitrogen and helium. The nitrogen molecule is normally much larger than the helium atom; at comparatively low pressures this shows itself in the larger molecular volume of nitrogen. But as pressure increases toward the upper end of the range, there remain more possibilities in the way of decrease of volume in the nitrogen molecule than in the helium atom. The more complicated structure remains the more compressible at the high pressures. In the same way the argon atom is a more complicated structure than the ammonia molecule, consisting of 19 extra nuclear electrons against 10, so that it would be expected to remain more compressible, and the crossing of the curves becomes plausible. For the same reason the curve of argon crosses that of hydrogen. Of course the pressure of the crossing is without absolute significance (as the zero at 3000 is without absolute significance), but the relative shape of the curves, which makes the crossing possible, is of absolute significance.

#### EQUATIONS OF STATE FOR HIGH PRESSURES.

There have been proposed a number of equations of state for gases, mostly on the basis of the work of Amagat,<sup>1</sup> and it is of interest to find how these agree, over a pressure range much wider than Amagat's, with the new experimental facts. Of course if an equation is to be used to extrapolate to infinite pressures, a use which has frequently



been made of the equations hitherto proposed, it must also be possible to extrapolate to 15000 with it.

In the first place, the classical equation of van der Waals,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

which was constructed specially to take account of the size of the molecules and the forces between them, and which would therefore seem to be especially adapted to use at high pressures, is known not to work at all, if for the constants of the equation we use the values determined in the regular way from the critical data. Thus the value listed in the Smithsonian Tables for "b" of hydrogen is  $880 \times 10^{-6}$ ; this is the theoretical volume at infinite pressure. But experimentally the volume assumes this value between 4000 and 5000 kg. For smaller volumes, corresponding to pressures greater than 5000, the formula demands negative pressures. Or stated in another way, van der Waal's equation predicts that under infinite pressure the volume will be that which we actually find under 4500 kg. This means that the actual gas under high pressures continues much more compressible than the equation indicates. It is, however, of interest to inquire whether the general form of van der Waal's equation cannot be maintained as an empirical equation with properly determined constants to give correctly the high pressure behavior. I have tried to do this for hydrogen. I have determined the *a* and the *b* of the equation above so as to agree with my experimental values at 3000 and 6000 kg. (this pressure range corresponds to more than half my volume range). With the constants so determined I have computed the volume to be expected at 13000 kg. This I find to be 8.06 cc. per gm. against 7.33 experimental, or expressed by differences, the decrease of volume between 3000 and 13000 demanded by the equations is 3.11 cc. per gm., whereas the experimental decrease is 3.76. The equation gives too large a volume (too small a compressibility) at high pressures, and is therefore not suitable, even when treated as a purely empirical equation with the constants so chosen as to fit the high pressure data. The fact that the "a" determined so as to fit the data at 3000 and 6000 is negative shows that the constants have no theoretical significance.

I have also tried an equation of simpler type than van der Waal's, which also represents the volume under infinite pressure as a finite quantity different from zero. This equation is

$$p(v - b) = CT.$$

The advantage of this equation is that it may be checked from a knowledge of only the changes of volume beyond a certain fiducial pressure, and does not require a knowledge of the actual volumes. This may be seen by writing it in the form  $p(v_0 - \Delta v - b) = CT$ , where  $v_0$  is the volume (unknown) under the fiducial pressure.  $\Delta v$  is known experimentally, so that the equation is still a two constant equation, treating  $v_0 - b$  as a new single constant, with  $p$  and  $\Delta v$  the experimental quantities to be substituted into it. I have used this as an interpolation equation, choosing the constants so as to reproduce the experimental volumes at 3000 and the maximum pressure, 13000 or 15000. The equation does not work for any of the gases; for hydrogen the experimental volume lies above that given by the equation over the entire intermediate range of pressure, for helium the experimental curve is below the equation for the first part of the pressure range and above it for the last, for ammonia the experimental curve is below that of the equation over the entire range, for nitrogen the experimental is also below the equation over the whole range, and for argon, the experimental is above the equation over the entire range. The discrepancies rise to as much as 25 or 30% of the volume change.

I have also tried to fit to the data for hydrogen a three constant formula, which at constant temperature is of the form:

$$(p + P)(v - b) = C.$$

A formula of this type has been applied by several investigators in the region of high pressures. Tumlriz<sup>13</sup> and Tammann<sup>14</sup> have applied it with considerable success to the data of Amagat for liquids to 3000 kg/cm<sup>2</sup>, and recently Richards<sup>15</sup> has extensively applied it to my measurements of the compressibility of metals<sup>16</sup> over a pressure range of 12000 kg/cm<sup>2</sup>. Tumlriz and Tammann differ as to the sort of function of temperature which they regard the "constants" to be, and Richards regards the formula as only a good approximation over a fairly wide pressure range, but recognizes that over a wider range both the  $P$  and the  $b$  of the formula are functions of pressure at constant temperature.

The three constants I determined so as to give the experimental volumes at 2000, 8000, and 13000 kg.; their values were:  $P = 2204$  (so-called internal pressure),  $b = 4.81$ , and  $C = 38200$ . The values shown in Table VII were found. It is seen that the experimental values lie below the calculated ones from 2000 to 8000, above them from 8000 to 13000, and of course below them again beyond 13000.

That is, this formula again gives a too small compressibility at the high pressures.

I believe that one reason for the failure of equations of this type is to be found in the compressibility of the atoms or molecules. The atoms probably have a rather small compressibility, but one which stays fairly constant over a very wide range of pressure. It results that over a small pressure range the volume of the atoms will appear

TABLE VII.

COMPARISON OF OBSERVED AND EXPERIMENTAL VOLUMES OF HYDROGEN.

Pressure kg/cm <sup>2</sup>	Volume cc. per gm.	
	Calc.	Exp.
2000	13.90	13.90
3000	12.16	11.64
4000	10.98	10.12
5000	10.12	9.80
6000	9.48	9.29
7000	8.96	8.87
8000	8.55	8.55
9000	8.22	8.26
10000	7.94	8.01
11000	7.70	7.78
12000	7.50	7.55
13000	7.32	7.32

to be invariable within the limits of experimental error, and may be treated as a constant in the equations, but over a larger pressure range the change of volume of the atoms becomes apparent.

Recently Professor F. G. Keyes has developed a type of equation from a theoretical standpoint,<sup>17</sup> and has determined the constants from the best data hitherto available. It is of interest to compare how the results calculated by his equations for high pressures agree with experiment.

It is especially to be kept in mind that the pressure in all the following formulas of Keyes is in atmospheres, and not in kg/cm<sup>2</sup>.

*Hydrogen.* Keyes' equation for hydrogen<sup>10</sup> is of the general type which he uses for all substances not monatomic, namely

$$P = \frac{R\tau}{v-\delta} - \frac{A}{(v-l)^2}$$

with the numerical values

$$\delta = 9.619e^{-\frac{2.898}{v}}, \quad A = 3.91 \times 10^4, \quad l = 1.18.$$

$P$  is the pressure in atmospheres, and  $v$  is the volume in cc. per gm. At 30° I find the following numerical values of volume approximately.

Pressure kg/cm <sup>2</sup>	Volume cc. per gm.	
	Calc.	Exp.
2523	12	12.3 (12.0)
3116	11	11.6 (11.3)
3879	10	10.7 (10.4)
4713	9.5	10.1 ( 9.8)
5622	9	9.5 ( 9.2)
8907	8	8.3 ( 8.0)
14000	7.32	7.2 ( 6.9)

I have given two sets of figures in the experimental column. The first are those given in Table I and are based on Amagat's value at 3000 kg. as fiducial. I have already explained that Keyes' volume at 3000 is less than Amagat's. The experimental figures in parentheses are corrected by a subtractive constant so as to make the fiducial volumes agree, affording a juster basis of comparison. It will be seen that the equation makes the gas initially more compressible and finally less compressible: again the compressibility of the gas persists at high pressures. This may be seen in another way from the equation, which predicts a limiting volume at infinite pressure of about 6. I do not believe that the experimental data give the impression of a limiting volume (if there is one at all) so high.

*Helium.* This gas, being monatomic, has a somewhat simpler type of equation,<sup>11</sup> namely

$$P = \frac{R\tau}{v-\delta} - \frac{A}{(v+l)^2},$$

where  $\delta = 3.17, \quad A = 3285.3, \quad l = 6.84.$

At 65° I find the following values:

Pressure kg/cm <sup>2</sup>	Volume cc. per mol.	
	Calc.	Exp.
3314	21.2	21.1
3894	20.0	19.4
4660	18.8	17.8
5802	17.6	16.1
7681	16.4	14.5
9764	15.6	13.4
11351	15.2	12.8
13495	14.8	12.1

It will be seen that the calculated volumes become continually greater than the experimental ones as pressure increases. This is the same behavior as shown by hydrogen; the compressibility persists.

It should be said that the constants in this equation for helium were deduced from measurements of Onnes to a maximum of 70 atmospheres. The domain of extrapolation is very wide; it is surprising that the equation works as well as it does.

*Ammonia.* Keyes' equation for ammonia<sup>18</sup> is

$$P = \frac{4.8177}{v - \delta} \tau - \frac{34610}{(v + 1.173)^2},$$

$$\log_{10} \delta = 0.9813 - \frac{3.08}{v}$$

This is based on results obtained at the Mass. Institute of Technology in 1912, reaching to very low pressures. This equation, with its constants determined by such data, appears fundamentally incompetent to represent the facts at pressures even moderately high. Thus at a molecular volume of 50 cc. per mol. the pressure has already turned negative.

*Nitrogen.* Keyes gives two equations for nitrogen. The first<sup>17</sup> is based on the data of Amagat between 100 and 1000 atmospheres, and is

$$P = \frac{2.9138}{v - \delta} \tau - \frac{1587}{(v - 0.007)^2}, \quad \text{where } \log_{10} \delta = 0.2200 - \frac{0.284}{v}.$$

At 68° I calculate the following values.

Pressure kg/cm <sup>2</sup>	Volume cc. per mol.	
	Calc.	Exp.
2444	36.5	38.1 (36.0)
3091	33.7	35.8 (33.7)
4201	30.9	33.1 (31.0)
5831	28.0	30.7 (29.6)
8390	25.3	28.5 (26.4)
12670	22.5	26.2 (24.1)
15502	21.1	25.3 (23.2)

The experimental values in parenthesis have been corrected by a subtractive constant to make the volume at 3000 agree with that calculated. My value at 3000 is derived from Amagat's experimental value at 3000, whereas the calculated value at 3000 employs Amagat's results to 1000. The discrepancy is to be attributed in part to inconsistency between Amagat's high and low pressure results, as already explained.

It is to be noticed that the formula works differently in the case of nitrogen than for hydrogen and helium, for here it gives too small volumes (too high compressibility) at the high pressures.

The second equation of Keyes<sup>19</sup> is based on measurements made at the Mass. Institute of Technology in 1923 by Taylor and Smith on very pure nitrogen, but over a much smaller pressure range. The equation is:

$$P = \frac{2.9286}{v-\delta} \tau - \frac{1623.6}{(v+0.2954)^2},$$

$$\log_{10} \delta = 0.18683 - \frac{0.3113}{v}.$$

This equation is not adapted at all to the high pressure measurements. Thus it predicts that a volume of 21.1 cc. per mol. will be found at a pressure of 5000 kg/cm<sup>2</sup>, whereas it will not be actually found at less than 25000, making a most conservative extrapolation. It is evident that the high pressure behavior contains features not sufficiently foreshadowed by the low pressure behavior.

*Argon.* Keyes' equation<sup>11</sup>, based on Crommelin's low pressure results, is:

$$P = \frac{2.0578}{v-1.278} \tau - \frac{995.7}{(v-0.247)^2},$$

Applied at high pressures, this indicates a very much too rapid falling off of compressibility. The calculated change of volume between 3000 and 12500 kg/cm<sup>2</sup> is 5.42 cc. per gm. atom against 8.18 experimental.

The general conclusion seems to be that this type of equation does not give an adequate method of predicting the behavior at high pressures from that at low. It would without doubt be possible to redetermine the constants in the equations so that the equation could be used as an interpolation formula over the entire range of pressure, but I believe that in view of the experience above, there would still be a good deal of question as to the chances of using the equation thus determined as an extrapolation equation to very much higher pressures.

I believe that the method of procedure here is to find a formula of a type such that when its constants are determined to fit the experimental values from 3000 to 6000 it will give correct values by extrapolation to 15000. Then if the constants are readjusted so as to cover the range 3000 to 15000 with slightly greater accuracy, we may extrapolate over a much wider range with considerable confidence. Furthermore, it is always to be borne in mind when attempting to construct such equations, that physically a sufficiently high pressure is to be expected to freeze the amorphous fluid phase to the crystalline solid.

*Becker's Equation for Nitrogen.* Recently Becker<sup>20</sup> has constructed from Amagat's data for nitrogen, on the basis of some theoretical considerations, an equation expressly designed to give the volume at pressures much beyond those of Amagat's experiment. The equation is

$$p = \frac{R\tau}{v} \left( 1 + \frac{\kappa}{v} e^{\frac{\kappa}{v}} \right) - \frac{a}{v^2} + \frac{\chi}{v^{\beta+2}}$$

Here  $p$  is in dynes/cm<sup>2</sup>, and  $v$  is in cc. per mol. The constants are:

$$R = 8.31 \times 10^7, \kappa = 40.3, a = 1.26 \times 10^{12}, \chi = 384 \times 10^{17}, \beta = 5.$$

This equation gives at 3000 the same volume which I have given above (as it should, because both of us connect with Amagat's data at 3000), and at higher pressures gives volumes very slightly less than those which I have found experimentally, the agreement being much closer than that of any other formula which I have tried. Thus at 15000 kg/cm<sup>2</sup>, the calculated volume is 25 against 25.4 experimental.

The formula contains four disposable constants, but perhaps this is not too many when it is considered that the ordinary critical behavior as well as the high pressure behavior is reproduced.

## SUMMARY.

A simple modification of the apparatus with which the compressibility of liquids was measured is described with which the compressibility of hydrogen, helium, ammonia, nitrogen, and argon has been measured to pressures varying from 12000 to 15000 kg/cm<sup>2</sup>. The changes of volume measured experimentally are from a fiducial pressure of 3000 as the zero. The results are shown in Tables and curves and various properties of the results are discussed. The compressibility under high pressures approaches that of ordinary liquids under the same pressures, and is much less than the compressibility of ordinary liquids at low pressures. The departure from a perfect gas is indicated by the behavior of  $p_v$ ; at 15000 kg. this is about 16 for nitrogen and 6 for helium.

The gaseous densities under the highest pressures are such that the molecules or atoms are very nearly in contact in the sense of kinetic theory. It is shown that the phenomena at high pressures probably depend on the compressibility of the atoms or molecules themselves; a complicated molecule like nitrogen retains more compressibility at high pressures than a simple atom like helium.

No general type of equation of state for high pressures has been yet proposed which agrees well with the facts. Becker's equation for nitrogen agrees much better than any of the others. The discrepancy between most of the equations and experiment is in such a direction that the actual volumes are smaller than the calculated volumes at high pressures. This is to be ascribed to the compression of the atoms.

Few satisfactory values were found for the thermal expansion of these gases, but it does seem highly probable that the expansion remains large under high pressure.

The data for gases enable a lower limit to be set on the compressibility of liquid and solid hydrogen and of liquid helium. It appears that these solids and liquids are very much more compressible than any hitherto measured.

It is a pleasure to acknowledge my indebtedness to my assistant Mr. H. B. Curry for many of the readings.

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